Response to ''Comment on 'From Rouse dynamics to local relaxation: A neutron spin echo study on polyisobutylene melts'''' [J. Chem. Phys. 113, 11396 (2000)]

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In the comment of L. Harnau[1] it is claimed that in contrast to our conclusion reported in Ref. 2 the intermediate single chain scattering function of PIB in the melt as obtained by neutron spin-echo spectroscopy (NSE) may be described by the semiflexible chain model. Our conclusion was that only an extra (internal) friction term can explain the observed relaxation behavior.

Now Harnau points out that the contour length, L, was given an inappropriate value. He displays a fit with $L=160$ Å and a persistence length of $l_p=1/(2p)=9$ Å.

Using exactly these values and the value of the line friction coefficient γ derived from the center-of-mass diffusion D_{CM} we compared the result obtained with the stiff chain theory described in Ref. 3. The diffusion coefficient follows directly from the low Q data $D_{CM}=1.54\pm0.16$ Å^2/ns leading to γ by using the relation $D_{CM}=k_BT/(\gamma L)$.

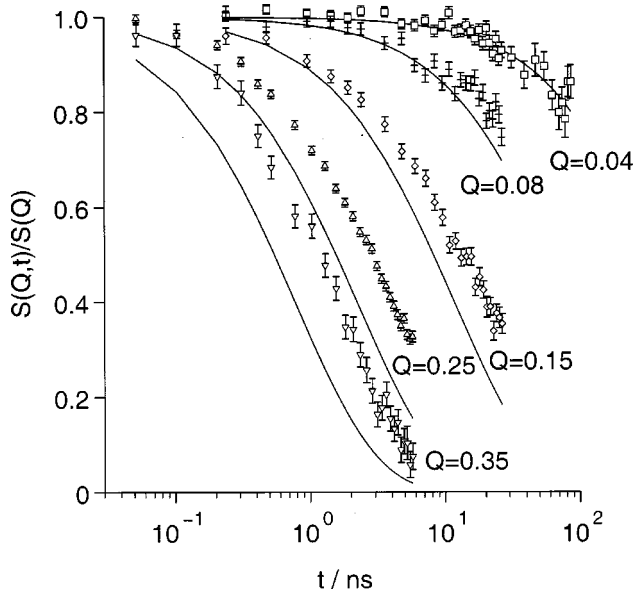

FIG. 1. $S(Q,t)/S(Q)$ measured for a hydrogenated PIB chain ($M_w=3.9$ K) in a deuterated PIB melt at $T=470$ K. The solid lines correspond to calculation of the stiff chain model with $L=160$ Å, $1/(2p)=9$ Å, and $\gamma=k_BT/(D_{CM}L)=38$ (N/m)/(m/s). The predicted relaxation dynamics at high Q is considerably too fast. The numbers at the curves indicate the respective Q-values in Å^{-1}.

Figure 1 shows that the NSE data $S(Q,t)/S(Q)$ are only described at very low Q (diffusion regime), at high Q significant deviations are revealed. The PIB chains relax much slower than predicted. The primary geometrical data, namely the chain dimension R_g

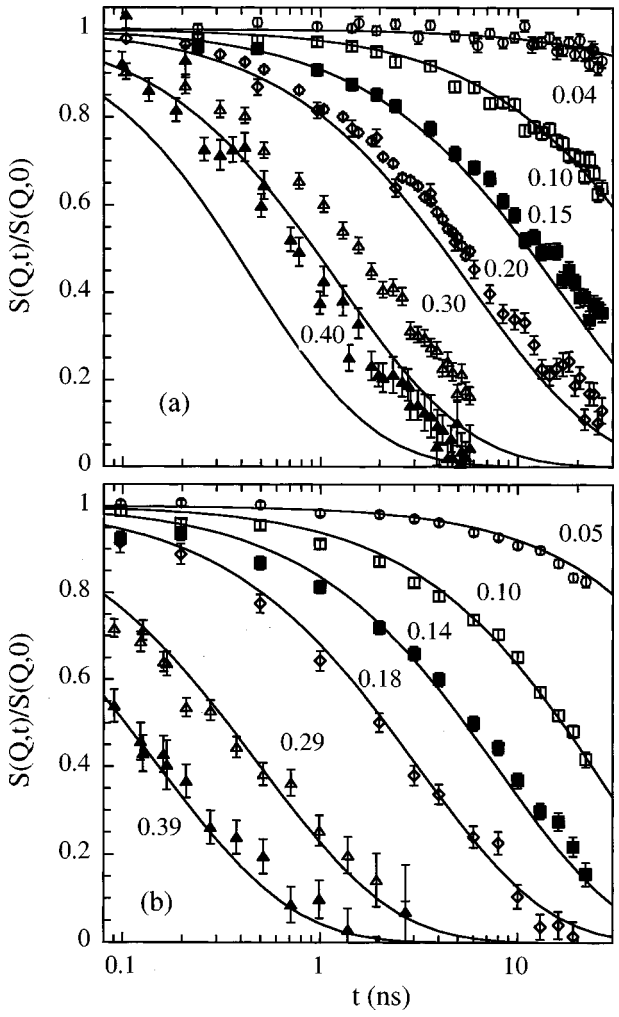

FIG. 2. Single chain dynamics $S(Q,t)/S(Q)$ measured for PIB chains at 470 K (a) and PDMS chains at 373 K (b) in the melts compared to the standard Rouse model (lines).

$=\sqrt{L/6p-1/4p^2+1/4p^3L-(1-e^{-2pL})/(8p^4L^2)}$ in terms of the low Q behavior of $S(Q)$ are fairly well described; however, at higher Q slight deviations from measurement indicate an overestimated stiffness. These results were carefully checked not to be prone to discretization errors in the numerical implementation; the used number of points of support along the chain (integrals containing eigenfunctions) as well as the number of modes considered is far beyond the point where influence on the results was detectable.

Since this discrepancy is disturbing one may wonder whether the numerical codes contain errors or are inappropriate. Therefore we add the results of a further experiment that without involved calculations corroborates the above result. In Fig. 2 we show the comparison of NSE data $(S(Q,t)/S(Q))$ obtained for PIB and poly(dimethyl siloxane) (PDMS) chains. The structural parameters for both chains are virtually identical, $R_g=19.2$ (21.3) Å, as well as the characteristic ratios $C_\infty=6.73\,(6.19)$, i.e., the polymers have nearly equal contour lengths L and identical persistence lengths. At the available experiment temperatures the diffusion coefficients and therefore the friction coefficients differ by a factor of 2; $D_{CM}(\mathrm{PDMS},T=373\ \mathrm{K})=2.7\ \text{Å}^2/\text{ns}$. Nevertheless, the comparison in Fig. 2 shows that the PDMS data [Fig. 2(b)] perfectly match with the prediction of the simple Rouse model[4] up to the highest Q-value, whereas the PIB data [Fig. 2(a)] show severe deviations from the Rouse model and (see above) to the stiff chain model. The different friction coefficient ξ resp. γ should simply scale the time axis (i.e., a simple shift operation of the shown log plots) both for the Rouse and the stiff chain models. As this is not the case, the conclusion is compelling that there must be an additional (internal) friction[2,5] present in PIB. The good description of the PDMS data by the Rouse model shows that chains with the given structural values are not yet stiff enough to exhibit discernible effects in $S(Q,t)/S(Q)$ due to their stiffness. The main difference between PIB and PDMS is the height of the internal potential barrier for local conformational transitions (about $3\cdots3.5$ kcal/mol, resp. $\simeq0.1$ kcal/mol). The delayed exploration of the conformational space due to the high barriers in PIB is thought to be the reason for the observed extra internal friction effects.

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